Enhanced carbonate dissolution:
a means of sequestering waste CO_2 as ocean bicarbonate

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Abstract

The reaction of a mineral carbonate, such as limestone, with water and CO_2 to form bicarbonate in solution, is explored as a CO_2 mitigation strategy. Initial cost estimates for such a process range from $18 to $128 per tonne CO_2 sequestered, with an energy penalty of about 8% and with relatively low environmental impact. The regional availability and transport of water and mineral carbonate appear to be the primary determinants of the strategy's cost and applicability. The bicarbonate-rich waste effluent would be released into rivers or coastal waters, ultimately adding a small amount to the existing, very large bicarbonate reservoir in the ocean. For many applications, this form of 'marine' carbon sequestration appears to be less costly, less affected by national and international regulations, more environmentally friendly and more effective over the long term than direct CO_2 injection into the ocean. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Given the steadily increasing atmospheric CO_2 burden caused by human activities and the potential this poses for climate modification [21,22], a variety of schemes to mitigate such increases have been proposed [17]. Among these have been chemical and biological methods of

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capturing CO_2 from waste gas streams and storing this carbon in forms or in locations isolated from the atmosphere. Examples include subterranean [14,19] and deep-ocean [16,29] injection of captured CO_2, biomass formation/accumulation on land or in the sea [8,23] and use of CO_2 as feedstock for the production of carbonaceous compounds [3,43]. Proposed chemical methods of sequestering carbon include CO_2 reactions with naturally or artificially formed alkaline compounds, such as silicates, oxides and hydroxides, generally leading to the storage of carbon ultimately in the form of solid carbonate [12,27,28]. Reactions involving solid carbonate dissolution or 'weathering' in the presence of water and CO_2 to form bicarbonate in solution are also thought to be capable of absorbing a significant fraction of the anthropogenic CO_2 input. However, under natural conditions, this process is expected to take millennia [2,31]. Here, we wish to consider artificially enhancing mineral carbonate dissolution as a way of sequestering significant quantities of CO_2 at a much accelerated pace. This would involve bringing mineral carbonate and water into direct contact with CO_2-rich waste gas effluent from centralized industrial or municipal sources; thus, at least partially, consuming CO_2 to form relatively innocuous and long lived cations and bicarbonate in solution which would directly or indirectly be added to the already large pool of these ions in the ocean.

2. Relevant chemistry

Carbonate weathering proceeds as follows:
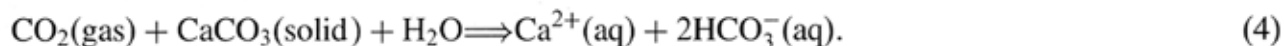
- gaseous CO_2 is dissolved in water;

$$CO_2(gas) \Longrightarrow CO_2(aq), \tag{1}$$

- and is subsequently hydrated to form carbonic acid;

$$CO_2(aq) + H_2O \Longrightarrow H_2CO_3(aq). \tag{2}$$

- The hydrated CO_2 is then reacted with a mineral carbonate (in this example, $CaCO_3$) to form Ca^{2+} and bicarbonate in solution;

$$H_2CO_3(aq) + CaCO_3 \text{ (solid)} \Longrightarrow Ca^{2+}(aq) + 2HCO_3^-(aq), \tag{3}$$

the net reaction being;

$$CO_2(gas) + CaCO_3(solid) + H_2O \Longrightarrow Ca^{2+}(aq) + 2HCO_3^-(aq). \tag{4}$$

While a wide range of metal carbonates can participate in such reactions, $CaCO_3$ and $MgCO_3$ and related complexes, such as $CaMg(CO_3)_2$, are the most abundant (especially as contained in calcite, limestone and dolomite) and, therefore, the largest participants in natural carbonate weathering.

However, rather than first diluting waste gas CO_2 in the atmosphere and then allowing reaction 4 to proceed naturally (and slowly) as it currently does, it would be advantageous to place water and mineral carbonate in direct contact with waste gas streams whose pCO_2 is commonly several orders of magnitude higher than that of the atmosphere (e.g., flue gas

$pCO_2 \cong 0.15$ atms [39] vs atmospheric $pCO_2 = 3.7 \times 10^{-4}$ atms [22]). This would allow $CO_2(aq)$ and carbonic acid (reactions 1 and 2) to form faster and in concentrations much higher than would naturally occur in water in contact with atmospheric CO_2. This elevation in acid concentration would promote reaction 3 and the formation of bicarbonate in solution, half of which would be derived from the original waste gas CO_2 (reaction 4). By analogy, enhanced mineral weathering reactions occur naturally in elevated CO_2 environments, such as in decomposing, organic rich soils and in the deep ocean [4,30]. We suggest that such reactions be emplaced at sites of high anthropogenic CO_2 emissions so as to attenuate their release to the atmosphere, at least partially.

3. Possible C_2SEA reactor parameters

We envision applying the CO_2 SequEstration as bicarbonAte (C_2SEA) process by allowing a CO_2-rich effluent gas stream to flow over or through a porous pile, bed or slurry of limestone (or other high $CaCO_3$ content) particles which are wetted by a continuous spray or flow of water. Referring to Fig. 1, a CO_2-rich gas stream (1) enters the reactor vessel (5) by one or more entry ways (e.g., 2, 3 and/or 4). The gas stream then passes over or through a wetted,
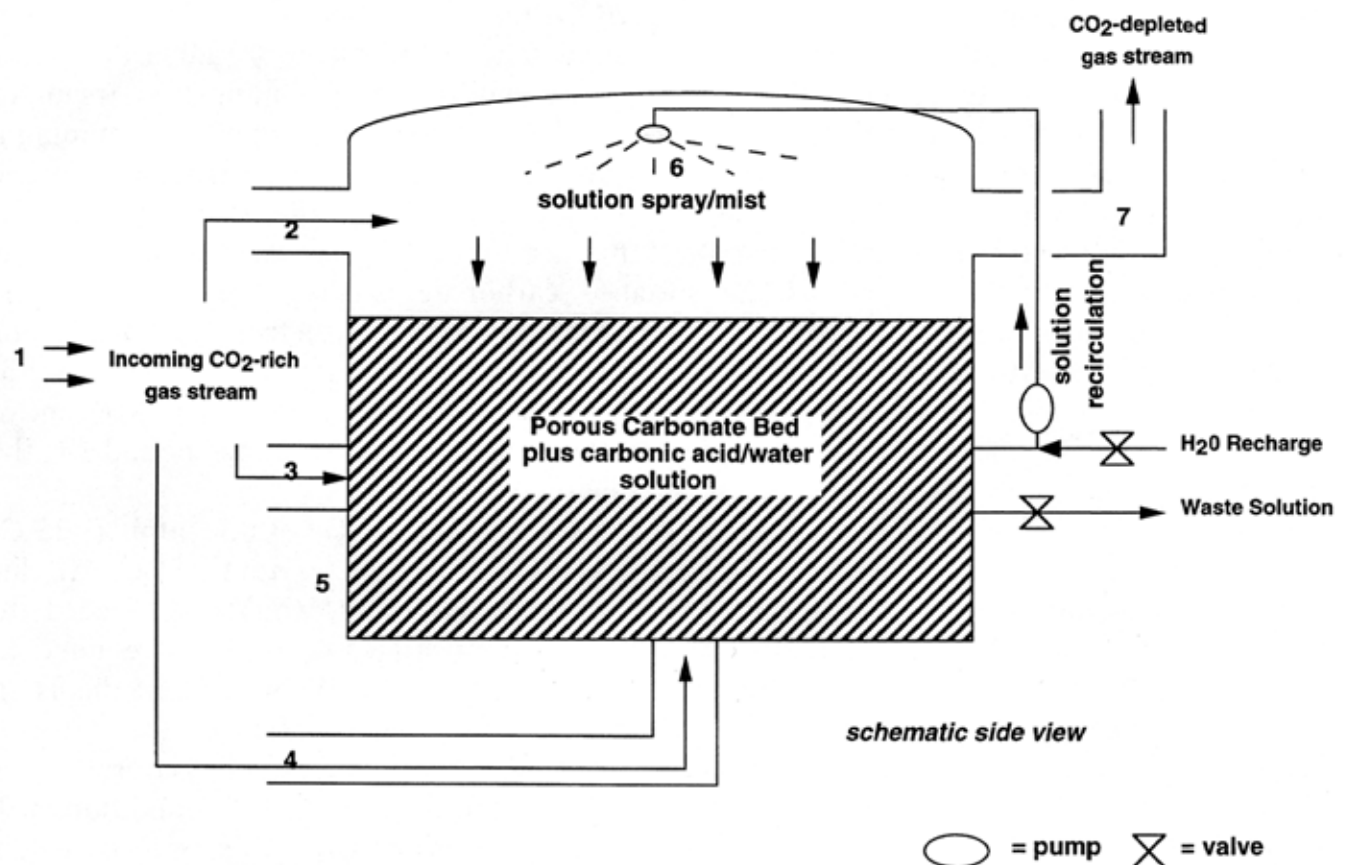

Fig. 1. An example of a possible C_2SEA reactor design.

porous bed of calcium carbonate (e.g., limestone) particles within the reactor. This carbonate mass is sprayed (6) and wetted with and partially submerged in a water/carbonic acid solution which is unsaturated with respect to bicarbonate ion. This arrangement exposes the incoming gas to a large surface area of water/solution in the form of droplets and wetted carbonate particle surfaces in (5), facilitating hydration of the entering CO_2 to form a carbonic acid solution within the reactor. CO_2-depleted gas then exits the reactor (7).

High-CO_2 waste gas is passed through such a reactor so as to contact the water and wetted surfaces, forming carbonic acid via reactions 1 and 2. The carbonic acid solution formed reacts with the carbonate to form calcium ions and bicarbonate in solution which is either recirculated or bled from the reactor and replaced with unreacted water within the reactor at a rate which maximizes benefit/cost. Assuming a waste gas pCO_2 of 0.15 atms (e.g., for coal-derived flue gas; [39]), the carbonic acid formed would then react with the calcium carbonate to produce HCO_3^- at a rate of roughly 2×10^{-6} mmols HCO_3^- cm^{-2} carbonate surface area s^{-1} ($\pm \sim 50\%$), if experiments with calcite in highly undersaturated solutions are representative [1,33]. Since half of this bicarbonate formation would be derived from waste gas CO_2 and the other half from the calcium carbonate, it would take 2.3 tonnes of calcium carbonate and 0.3 tonnes of water to react 1 tonne of CO_2 to form 2.8 tonnes of HCO_3^- in solution. Sequestering 1 tonne of CO_2 per day by this method would then require some 10^4 m^2 of carbonate surface area assuming the above bicarbonate formation rate.

If spherical carbonate particles are assumed, it can be shown for $CaCO_3$ [42] that $A = k \, t/r$ where A = the carbonate surface area in m^2, t = $CaCO_3$ mass in tonnes, r = particle radius in m and $k = 1$ m^3 tonne^{-1}. By specifying uniformly sized spherical particles of radius 10^{-2} m, it would then be necessary to present 100 tonnes of carbonate to the incoming gas stream to effect a sequestration of 1 tonne CO_2/day, affording a pile lifetime of roughly 40 d. Assuming a rhombohedral packing of spherical carbonate particles with a resulting total carbonate particle surface area/packed volume, A/V, of 222 m^2/m^3 ($= 2.22$ m^3 m^{-3} r^{-1}), the minimum required pile volume is about $(10^4$ m$^2)/(222$ m^2 m$^{-3}) = 45$ m^3 per tonne CO_2 sequestered day^{-1}. This required pile volume will decrease as the specified carbonate particle size decreases, the heterogeneity in particle size increases and as particle shapes deviate from a sphere. For example, Walter and Morse [42] found that natural calcium carbonate A/V can be several orders of magnitude higher than that predicted from spherical particles, thus for a given mean carbonate particle size, the preceding estimation method should yield an upper bound for the reactor bed volume.

Water in equilibrium with calcium carbonate and CO_2(gas) at a pCO_2 of 0.15 atms ($\sim 25°C$) will contain 6.7×10^{-3} molar bicarbonate [9] or 4×10^{-4} tonnes HCO_3^-/tonne H_2O. At this concentration, a minimum discharge of 7×10^3 tonnes H_2O/day would be needed to accommodate the above production and discharge of 2.8 tonnes HCO_3^- day^{-1} as required to sequester 1 tonne CO_2(gas) day^{-1} from the original waste gas stream. We stress that this is an absolute minimum H_2O requirement per tonne CO_2 sequestered because the rate of bicarbonate formation will decline (nonlinearly) to zero as bicarbonate saturation is approached [32], making it unlikely under practical application that equilibrium conditions will be attained. This means that the reactor bicarbonate concentrations will be likely to be below bicarbonate saturation prior to discharge, requiring a higher water flow rate through the reactor in order to accommodate the discharge of 2.8 tonnes HCO_3^- day^{-1}. For example,

attaining a ~~half~~ 3/4-saturated bicarbonate concentration (5×10^{-3} molar) would increase the above water requirement to 10^4 tonnes H_2O tonne^{-1} CO_2 sequestered day^{-1}. By comparison, we note that coal fired power plants consume roughly 800 tonnes H_2O per tonne coal burned [34] or about 400 tonnes H_2O per tonne CO_2 produced. However, reusing this 'free' water as the sole source of C_2SEA reactor water would allow a sequestration of about 4% of the CO_2 produced in coal fired electricity generation. Such a quantity is not trivial, given policies, e.g., the Kyoto Protocol, calling for only small fractional reductions in CO_2 emissions.

4. Water considerations

With the relatively high water demand of the C_2SEA process, it is likely that water availability and cost could, in many instances, determine the practical amount of CO_2 mitigation that can be effected for a given point source. No-cost water sources, such as power plant cooling water or other sources of recycled or reclaimed water, together with river or seawater—if available—should, therefore, be considered first. The use of seawater is particularly attractive for coastal power plants because: (i) there is virtually a limitless source of such water; (ii) carbonate dissolution is enhanced over that in freshwater due to increased ionic strength and (iii) bicarbonate waste can be directly dumped and diluted in the ocean.

Regarding (iii), we point out that, barring drainage into a landlocked basin, the ocean would be the ultimate repository of the bicarbonate and Ca^{2+} generated by C_2SEA, where 42×10^{12} tonnes of C are already present as dissolved bicarbonate plus a much smaller quantity of dissolved carbonate ion [5]. By comparison, if it were somehow possible to 'bicarbonate' the entire yearly global fossil fuel CO_2 emission (22×10^9 tonnes CO_2/y [24]), this would only annually add about 0.1% to the ocean's bicarbonate burden, while processing an amount of water equivalent to less than 0.02% of the ocean's volume. The availability of calcium carbonate for C_2SEA also does not appear to be an issue. The carbon mass of sedimentary carbonates is estimated to be 6×10^{16} tonnes [5] with a current mining output of roughly 10^9 tonnes crushed limestone per year for the US alone [41], enough to react about 4×10^8 tonnes CO_2/y using C_2SEA. We also note that the majority of anthropogenic CO_2 emissions in the US occur in the eastern half of the country [39], fortuitously coinciding with the majority of the nation's limestone reserves and production [40], and thus minimizing the limestone (or CO_2) transportation distances to C_2SEA potential facilities in this region.

5. Reactor effluent

While no US federal regulations currently exist regarding bicarbonate in wastewater, the 'hardness' and total dissolved solids load of C_2SEA effluent could limit the disposal of such waste into inland waterways which would ultimately deliver the bicarbonate to the ocean. Coastal power plants would again be at an advantage, where direct dumping of 'hard' C_2SEA effluent to the ocean would likely be unrestricted. This could pose a distinct advantage over proposed open-ocean CO_2 injection which would not be immune to international law, e.g., the London Dumping Convention [25]. Also, the ecological impacts of C_2SEA effluent are likely to

Table 1
Estimated cost per tonne CO_2 sequestered using a C_2SEA reactor (e.g., Fig. 1) in various scenarios[a]

	Rail transport of carbonate		Ship/barge transport of carbonate	
	$	+ 'Free' H_2O, $	$	+ 'Free' H_2O, $
Requirements:				
$CaCO_3$—2.3 tonnes limestone@$4.00/tonne	9.20	9.20	9.20	9.20
crushing@9kWh$_e$/tonne@$0.07/kWh$_e$	1.45	1.45	1.45	1.45
150 km transport via: rail@$0.035 tonne^{-1} km^{-1}	12.08	12.08		
ship/barge@$0.007 tonne^{-1} km^{-1}			2.42	2.42
H_2O—10^4 tonnes@$0.01/tonne	100.00		100.00	
or 'free' water		0.00		0.00
pumping cost, 57 kWh$_e$@$0.05/kWh$_e$	2.85	2.85	2.85	2.85
Capital, operation, and maintenance costs—capital cost, $50 M@$0.04$M^{-1} tonne^{-1} CO_2	2.00	2.00	2.00	2.00
O&M, 25% of capital cost	0.50	0.50	0.50	0.50
Total cost/tonne CO_2 sequestered	128.07	28.07	118.41	18.41

Other large-scale CO_2 sequestration technologies—$24 to $180
Direct CO_2 disposal in ocean—$90 to $180
Suggested CO_2 trading price or tax = $50 (and current Norwegian carbon tax)

[a] Carbonate cost from USGS [41]. Crushing costs derived by specifying a particle radius reduction from 10^{-1} to 10^{-2} meters and using the energy estimation equation 10-49 of Boyce [6], with an assumed electrical energy use efficiency of 40%. Energy cost here assumes offsite electrical energy consumption [18]. Per km $CaCO_3$ transportation costs: rail [20]; ship/barge = 20% of rail cost [26]. Required water volume assumes reactor effluent bicarbonate concentration of 5×10^{-3} molar (50% saturation). Per tonne water cost typical of agricultural water. 'Free' water refers to sources, such as seawater, power plant waste cooling water, river water, or other types of no-cost, untreated water. Water pumping cost assumes water must be pumped a total of 1.2 vertical meters (with or without water recycling through reactor) at 60% efficiency using equation 20-13 of Snow et al. [36]. Per kWh$_e$ cost here assumes onsite power usage and, therefore, excludes $0.02 power distribution cost added to kWh$_e$ energy cost for crushing (above). Capital costs are calculated by assuming a capital outlay of $50 M for an onsite power plant C_2SEA reactor and a payback rate of $0.04 $M^{-1} tonne^{-1} CO_2 sequestered [18]. Operating and maintenance costs are assumed to be 25% of capital costs [18]. Costs of other large scale CO_2 sequestration technologies from Herzog et al. [18] and Fujioka et al. [15]. See text for further details.

be far smaller than those predicted/observed for direct marine CO_2 dumping and resulting ocean acidification [10,38] because a substantial amount of waste CO_2 (and acidity) will have been neutralized to bicarbonate in the C_2SEA process.

The residual CO_2 concentration in C_2SEA effluent would nevertheless pose a problem. Returning to the above solution resulting from the equilibrium among water, calcium carbonate and CO_2 ($pCO_2 = 0.15$ atms, $T = 25°C$), such C_2SEA effluent would have a pCO_2 about 400 times above ambient air. This pCO_2 dichotomy between the effluent and air would lead to a rapid degassing of CO_2 from the former solution, causing carbonate ion oversaturation and likely precipitation of solid carbonate from the solution. Such effects could be minimized by direct dumping of the effluent into the ocean, allowing copious subsurface mixing and dilution of the effluent. By our calculation, a 100-fold dilution of the above reactor effluent, followed by complete CO_2 equilibration with the atmosphere, would lead to only a 13% increase in carbonate ion concentration in the resulting seawater. Such an increase would be unlikely to cause a carbonate precipitation event, given the already supersaturated state of the ocean as apparently maintained by certain naturally occurring ions in seawater which inhibit carbonate precipitation [30]. Depending on the relative ionic burden in C_2SEA effluent, it could be denser than the receiving water, causing the effluent to sink, further minimizing contact with and CO_2 loss to the atmosphere. The possibility for dilution/sinking would be more limited in inland waterways where undesirable effluent CO_2 degassing prior to sufficient wastewater dilution and/or prior to entry to the sea could result in in-stream carbonate formations analogous to travertines [13]. It may be possible to reduce such effects in freshwater by combining C_2SEA effluent with other wastewater streams whose ion and organic content inhibit carbonate precipitation from the effluent in the face of inadequate dilution and significant CO_2 degassing.

6. Cost and energy penalty estimates

With the preceding considerations and limitations in mind, our preliminary calculation of cost per tonne CO_2 sequestered using C_2SEA technology ranges from about $18 to $128 (Table 1). By comparison, recent cost estimates of CO_2 capture, transport, and open ocean injection range from $90 to $180/tonne CO_2 [15]. Significant cost savings for the C_2SEA scheme can be achieved through the use of 'free' sources of water, such as seawater, river water, or power plant cooling water, as well as the use of ship or barge transport of carbonate. The 'free' water scenario costs are significantly below the $50 tonne CO_2 tax currently levied in Norway (Table 1), suggesting that such a C_2SEA scheme might be an economically competitive CO_2 mitigation strategy.

In our estimates, we have included the cost ($1.45) and energy penalty (21 kWh_e) of crushing 2.3 tonnes of limestone (particle radius reduction from 10^{-1} to 10^{-2} m), as well as pumping the required water the equivalent of 1.2 vertical meters at 60% pump efficiency ($2.85 and 57 kWh_e, respectively). This amount of energy is envisioned for pumping the water to and from the site as well as internal water recycling. It could also include short distance pumping of the gas stream to/from/within the reactor if required. We, therefore, calculate an energy penalty of roughly 77 kWh_e/tonne CO_2 sequestered (not considering the energy used in carbonate

transport). If the combustion of 1 tonne of coal produces 2 tonnes of CO_2 and 2×10^3 kWh$_e$ [39], then this C$_2$SEA energy penalty amounts to about 8% of the energy produced. Herzog et al. [18] list energy penalties for CO_2 capture technologies alone (without disposal or sequestration), ranging from 13% to 37%. However, all of our cost and energy penalty estimates for C$_2$SEA should be viewed as preliminary and will vary widely depending on the desired reactor size, configuration and performance, the proximity to and cost of carbonate and water sources and the realized carbonate dissolution and CO_2 sequestration rates.

7. Other issues and alternatives

Regarding the actual rates of C$_2$SEA sequestration, experiments with impure calcium carbonate minerals (e.g., dolomite) yield dissolution rates lower than those of calcite [11]. However, we are unaware of any rate measurements conducted on more C$_2$SEA-relevant limestone, or on carbonate dissolution in highly CO_2-supersaturated seawater (pCO$_2 > 0.01$ atm). Factors negatively affecting such rates could include the presence and interaction of ions, such as SO_4^{2-} and PO_4^{2-} and certain metals, which can impede or inhibit dissolution [30]. If such effects are present, it may be necessary to offset them by: (i) increasing the reactor's carbonate surface area by decreasing the carbonate particle size or increasing the carbonate bed volume; or (ii) reducing the concentration or reactivity of contaminants from the incoming gas, carbonate, and/or water streams. The possible need for flue gas desulfurization (FGD) prior to the C$_2$SEA process could be one example. However, because FGD also commonly employs wet limestone (to convert SO_2(gas) to $CaSO_4$(solid) [37]), possible integration of such FGD and C$_2$SEA processes might be considered. While wet limestone FGD differs from C$_2$SEA in at least three important areas (it generates CO_2, it consumes O_2 and it produces a solid byproduct), the practical design and implementation of C$_2$SEA reactors could, nevertheless, benefit from models developed for the former process [7].

It may also be advantageous to increase the carbonate dissolution rate by maximizing the production and concentration of carbonic acid in the reactor solution. This could be achieved by elevating the pCO$_2$ of the incoming waste gas stream, either by mechanically elevating the total gas pressure within the reactor or by pre-concentrating the CO_2 contained in the incoming gas stream using various existing technologies [17]. Under circumstances where CO_2 emissions are far from water and carbonate resources, the overland piping or shipping of concentrated gaseous or liquid CO_2 to a centralized C$_2$SEA reactor (rather than the transport of carbonate and water to the site of CO_2 generation) might prove cost effective at rates below \$0.01 tonne^{-1} CO_2 km^{-1} [35]. Also, to the extent that the hydration rate of CO_2 (reactions 1 and 2) limits the carbonate dissolution rate in the reactor, it may be appropriate to add the highly effective catalyst carbonic anhydrase to the reactor solution. The cost/benefit of the above potential reactor modifications needs to be investigated.

8. Summary and conclusions

The C$_2$SEA approach appears to have some advantages over other large scale CO_2

sequestration technologies proposed to date. First, unlike other chemical CO_2 capture methods (e.g., those using monoethanol amine or highly alkaline solutions), the process does not require exotic, expensive, or environmentally damaging reactants or procedures. While in some cases regionally scarce, the C_2SEA reactants, water and calcium carbonate, are globally abundant, inexpensive and innocuous. The reactor would have a relatively low energy penalty, incurred primarily in reactant transport to and within the reactor. The reactor waste products, Ca^{2+} and bicarbonate, are relatively benign and, once in the ocean, will add little to the burden of these ions already present. Coastal dumping of fossil carbon in the form of bicarbonate appears to have economic, ecological and legal advantages over direct, open ocean CO_2 injection. Furthermore, the lifetime of carbon stored as marine bicarbonate will be substantially longer than carbon injected as CO_2 into the subsurface ocean, Caldeira and Rau [44]. The C_2SEA method would circumvent the risk of significant CO_2 degassing inherent in direct subterranean and submarine CO_2 injection and storage. We believe that the efficacy and economics of the C_2SEA process in partially sequestering CO_2 from the atmosphere on an industrial and possibly global scale deserves further study.

Acknowledgements

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